

AD-A141 184 THE VAPOR PRESSURE OF SALT-HCl-WATER SOLUTIONS BELOW OC 1/1  
(U) MACKAY SCHOOL OF MINES RENO NV DEPT OF CHEMICAL AND  
METALLURG... E MILLER JAN 84 AFOSR-TR-84-0343

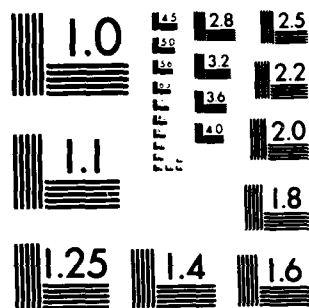
UNCLASSIFIED AFOSR-82-0049

F/G 7/4

NL



END  
DATE  
FILMED  
6-84  
DTIC



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A



APOSR-TR. 84-0343

(4)

# UNIVERSITY OF NEVADA RENO

Department of Chemical and  
Metallurgical Engineering  
Markay Building  
University of Nevada  
Reno, Nevada  
97502-0000

January, 1984

Annual Report Covering Period 1 Dec 83 to 30 Nov 83

Prepared by: [illegible]

Prepared by: Eugene M. [illegible]

Work performed by: Eugene M. [illegible]

Contract Grant: AFOSR-ET-8049

MAY 17 1984  
A

Order for: AIR FORCE OFFICE OF SCIENTIFIC AND TECHNICAL INFORMATION  
Building 400  
Randolph AFB, TX 78150  
Attn: Mr. Leonard M. [illegible]

Approved for public release; distribution unlimited.

Qualified requesters may obtain additional copies from the  
Defense Documentation Center; all others should apply to  
the National Technical Information Service.

Reproduction, translation, publication, use and disposal in  
whole or in part by or for the United States Government is  
permitted.

AD-A141 184

DTIC FILE COPY

84 05 15 236

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER <b>AFOSR-TR- 84-0343</b>	2. GOVT ACCESSION NO. <b>AD-A242184</b>	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle)  <b>THE VAPOR PRESSURE OF SALT-HCl-WATER SOLUTIONS BELOW OC</b>		5. TYPE OF REPORT & PERIOD COVERED  <b>INTERIM 1 Dec 81 - 30 Nov 83</b>
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s)  <b>Eugene Miller</b>		8. CONTRACT OR GRANT NUMBER(s)  <b>AFOSR 82-0049</b>
9. PERFORMING ORGANIZATION NAME AND ADDRESS  <b>UNIVERSITY OF NEVADA RENO MACKAY SCHOOL OF MINES RENO, NV 89557</b>		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS  <b>2308 B1 61102F</b>
11. CONTROLLING OFFICE NAME AND ADDRESS  <b>AIR FORCE OFFICE OF SCIENTIFIC RESEARCH/NA Bolling AFB, D.C. 20332</b>		12. REPORT DATE  <b>Jan 84</b>
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES  <b>5 plus 4 figures</b>
		15. SECURITY CLASS. (of this report)  <b>UNCLASSIFIED</b>
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)  <b>Approved for public release; distribution unlimited.</b>		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)  <b>THERMOCHEMISTRY, VAPOR PRESSURE, SOLUBILITY, CaCl<sub>2</sub>-HYDROCHLORIC ACID</b>		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  <b>Vapor-liquid equilibria data are presented for hydrochloric acid solutions, ranging in nominal HCl mol fraction from 0.11 to 0.23, saturated with CaCl<sub>2</sub> at nominal temperatures between 0 and -40 C. Total pressures were measured by capacitance gauges, vapor compositions by direct vapor-phase sampling into a quadruple mass filter and liquid compositions by electric conductivity.</b>		

# ABSTRACT

↙ Vapor-liquid equilibria data are presented for hydrochloric acid solutions ranging in nominal HCl mol fraction from 0.110 to 0.225, saturated with  $\text{CaCl}_2$ , at nominal solution temperatures between 0 and  $-40^\circ\text{C}$ . Total pressures were measured by capacitance gauges, vapor compositions by direct vapor-phase sampling into a quadrupole mass filter and liquid compositions by electric conductivity. The addition of  $\text{CaCl}_2$  to hydrochloric acid breaks the azeotrope and generally increases the vapor pressures of HCl and water.

Solubility and solution densities have also been measured. Solution compositions have not been completed up to limiting the interpretation of the results to some extent. These are presently being done. It is probable that the effect of  $\text{CaCl}_2$  on the formation of secondary smoke in a reduced smoke rocket plume has less an effect than  $\text{NaCl}$ . ↗



A-1-23

## INTRODUCTION

The vapor pressures of hydrochloric acid solutions are important to the modelling of secondary smoke in reduced smoke ammonium perchlorate solid propellant rocket plumes, ref 1, since the growth of secondary smoke droplets is dependent on their equilibrium behavior. In addition, the behavior of strong electrolytes in aqueous solution is of fundamental theoretical interest. Inorganic salts dissolved in hydrochloric acid will significantly modify its equilibrium behavior due to their effects on the activities of the HCl and water in the liquid phase, ref 2. The resulting change in the solution vapor pressure alters the rate of formation and the chemical composition of the secondary smoke, refs 3, 4. The major contaminants found in ammonium perchlorate are sodium and potassium salts. In addition, trisodium phosphate added to ammonium perchlorate for ease in processing provides a major source of soluble electrolyte. All these cations are found in the rocket plume in sufficient quantity to nucleate the secondary smoke droplets, and to subsequently dissolve and influence the dynamics of growth and the chemical composition of the smoke, ref 5. If iron and copper combustion modifiers are avoided, none of the others commonly added to propellants will produce salts soluble enough to effect significant changes in the behavior of the hydrochloric acid smoke droplets. The original choices of NaCl and  $\text{CaCl}_2$  as the salts for study were based on these considerations as well as for their differences in ionic strength. A very limited study of HCl was subsequently added for consideration but time did not permit actual experimental measurements to be made.

Prior to the measurements made by the principal investigator under sponsorship of AFOSR, no vapor pressure data were available for either pure hydrochloric acid or for hydrochloric acid containing dissolved NaCl or  $\text{CaCl}_2$  for temperatures below 0C, the temperatures of primary interest for secondary smoke formation. Data exist for these solutions, either primary vapor pressure or activities from which the vapor pressure may be predicted, only for temperatures at or above 0C. The low temperature vapor-liquid equilibria measurements for the pure hydrochloric acid and for solutions containing NaCl have been completed and are published in refs 6 and 7. The experimental vapor-liquid equilibria of  $\text{CaCl}_2$ -HCl- $\text{H}_2\text{O}$  solutions for nominal temperatures from 0 to -40C are given in the present report completing the study of the pure and salted hydrochloric acid solutions.

## EXPERIMENTAL

As shown schematically in Figure 1, a 2-liter Pyrex flask is immersed in a methylene chloride bath cooled by a two-stage mechanical refrigeration system. The temperature of the bath is maintained within  $\pm 0.1^\circ\text{C}$ , monitored by a calibrated platinum resistance thermometer. Removal of air from the system is accomplished by a mechanical vacuum pump in series with a liquid nitrogen trap. Pressures are measured with two M.S. Baratron Type 220 gauges ( $10^{-4}$  to 1 torr, and 1.02 to 1015 torr) calibrated by the manufacturer by means of a FEO air dewar gas meter and a transfer standard to  $\pm 0.01\%$  full range. For analysis of liquid solution samples, the acid in the sample is distilled away from the salt in a closed glass system. All water of hydration of the  $\text{CaCl}_2$  is driven off with the acid by heating the remaining salt to  $210-240^\circ\text{C}$ . The distilled acid and the salt subsequently dissolved in water are analyzed to  $\pm 1\%$  maximum standard deviation using a Barnstead Model RM-700K electroconductivity bridge and a Yellowstone YSI 3400 Pyrex cell in conjunction with standardized solutions.

Vapor pressures are measured for samples drawn from the vapor chamber into a Varian VGA-100 quadrupole mass filter. The ratio of partial pressures of water to  $\text{HCl}$  is determined from the recorded mass spectra in the range of 14-20 and 34-40 mass numbers. The mass spectra are obtained at mass filter pressures of nominally 3-6  $\times 10^{-6}$  torr sampling continuously from the vapor chamber which is open to the solution flask while pumping on the mass filter with a Varian 20-liter per sec Vacuon pump. The experimental procedure for determining the relative sensitivity of the mass filter to water and  $\text{HCl}$  as a function of composition, and the details of operation of the equipment for the vapor-liquid equilibrium measurements are given in ref 6.

## RESULTS & DISCUSSION

Liquid phase analyses have not been completed at this date and therefore the acid compositions given are nominal salt-free mol fractions and the salt concentrations are noted only as being "saturated". Total pressure,  $P$ , partial pressures of  $\text{HCl}$  and water,  $P_{\text{HCl}}$  and  $P_{\text{H}_2\text{O}}$  respectively, as

a function of salt-free mol fraction of HCl,  $X_{HCl}$ , and solution temperature,  $T$ , for solutions saturated with  $CaCl_2$  are given in Figures 2, 3, and 4 respectively. It may be noted from Figure 2 that the minimum pressure azeotrope observed for both the pure hydrochloric acid and for hydrochloric acid containing dissolved NaCl does not occur for the  $CaCl_2$ -HCl-water system. This is expected since  $CaCl_2$  is used commercially to break the azeotrope for the production of concentrated hydrochloric acid. Along with the disappearance of the azeotrope there is observed a steep pressure gradient between the  $X_{HCl}$  values of 0.110 and 0.125 such that the total pressure increases by an order of magnitude and the total pressure at  $X_{HCl} = 0.128$  is only moderately lower than the total pressure at 0.147. The total pressures in this range are an order of magnitude higher than those for pure hydrochloric acid or for acid in which NaCl is dissolved. Additionally, it may be seen in Figure 3 that the partial pressure of HCl increases markedly in the same  $X_{HCl}$  range, HCl vapor mol fractions being 20.92. The HCl partial pressures are also at least an order of magnitude higher than those of pure and NaCl-hydrochloric acid solutions in this range of  $X_{HCl}$  values. Figure 4 illustrates the variation of the water vapor pressure with temperature and  $X_{HCl}$ . The water vapor pressures in the  $X_{HCl}$  range 0.128 to 0.147 appear to be higher than those for pure or NaCl-hydrochloric acid solutions. It may be noted also that the  $CaCl_2$  solution at  $X_{HCl} = 0.147$  freezes at a higher temperature than either the pure or NaCl-saturated hydrochloric acid solutions. Further interpretation of the vapor-liquid results and reporting of the  $CaCl_2$  solubility in hydrochloric acid as a function of acid concentration and temperature await completion of the solution analyses.

Based on related computations reported in ref 5, it appears from these data that  $CaCl_2$  present in the reduced smoke rocket plume will not cause as serious an effect on the formation of secondary smoke as would NaCl and probably KCl. Confirmation of this conclusion must await completion of the solution analyses and secondary smoke prediction computations for atmospheric and flight conditions of interest.

#### FUTURE PLANS

Although the contractual period of the grant has expired and the funds expended, the solution analyses presently



underway for the hydrochloric acid and  $\text{CaCl}_2$  will be completed and made available to AFOSR at no additional cost to AFOSR. Subsequently, a manuscript summarizing the results of the study of the  $\text{CaCl}_2$ -HCl-water system will be submitted to an archive journal for publication.

#### REFERENCES

- (1) Miller, E., "Smokeless Propellants," Chap. 15; "Fundamentals of Solid Propellant Combustion," Lee, K. and M. Summerfield, eds. Progress in Aeron and Astronautics, AIAA, in printing.
- (2) Harned, H.S. & B.B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold (1958)
- (3) Hoshizaki, H. et al, "Plume Visibility Detection Study," Report AFRL-TP-78-32, Vol. I, (Nov 78)
- (4) Miller, E., J.W. Connaughton & L.B. Thorn, "Measured and Predicted Laser Attenuation Through a Solid Rocket Plume," JANNAF Propulsion Meeting (1980)
- (5) Miller, E., "Comparison of Experimental & Predicted Secondary Smoke Optical Signal Attenuation," 13th JANNAF Plume Technology Meeting (1982)
- (6) Miller, E., "Vapor-Liquid Equilibria of Water-Hydrogen Chloride Solutions Below 0C," J. Chem. Eng. Data 27, 161-67 (Oct 83)
- (7) Miller, E., "Vapor-Liquid Equilibria of Hydrogen Chloride-Sodium Chloride-Water Solutions Below 0C," Submitted for publication to J. Chem. Eng. Data.

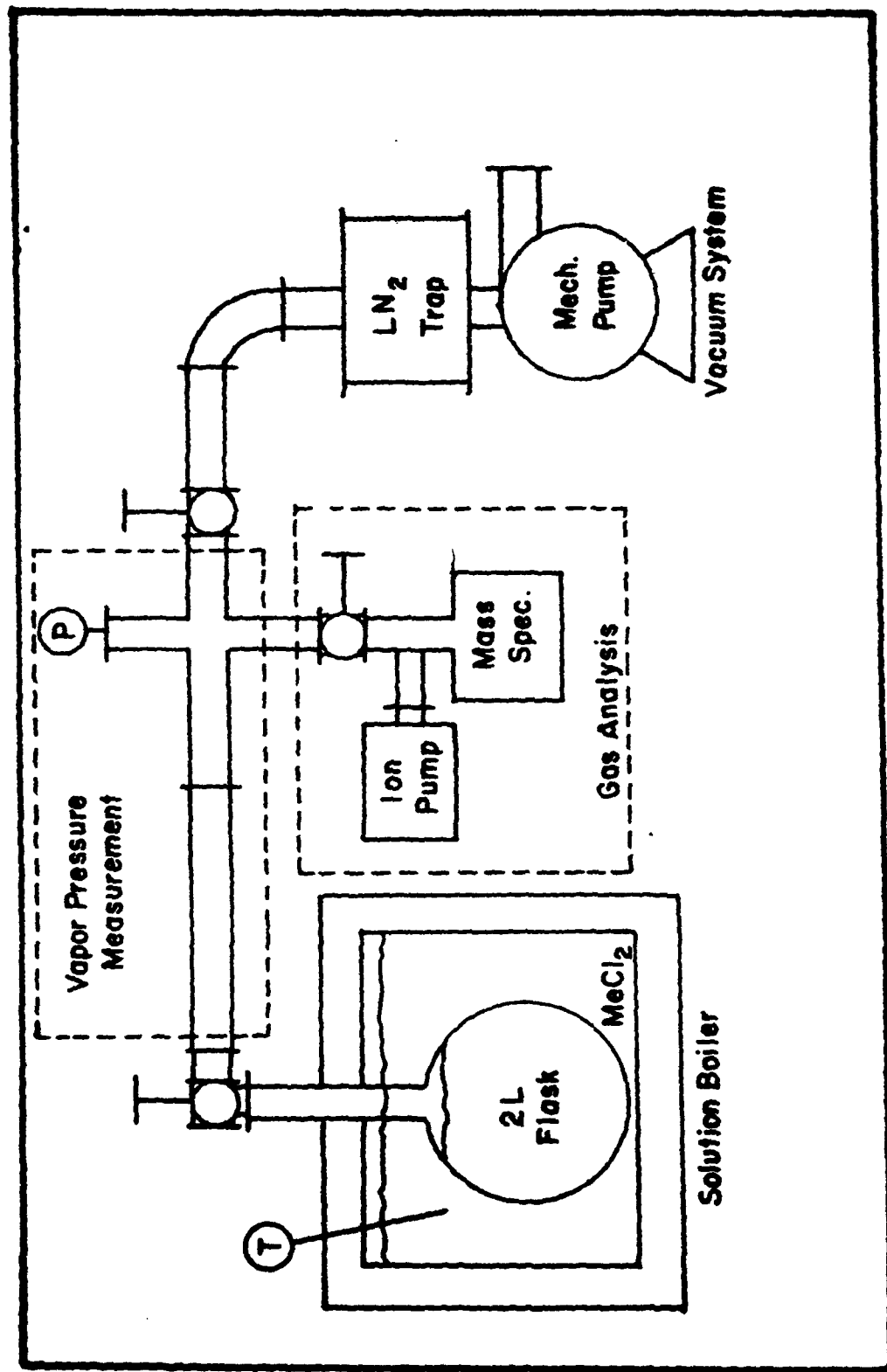


FIGURE 1  
Schematic of Experimental Apparatus

100:10

FIGURE 2

Sat'd  $\text{CaCl}_2$ -HCL- $\text{H}_2\text{O}$  Soln.  
 Total Pressure, P  
 vs  
 Temperature, T,  $^\circ\text{C}$   
 Mol Fraction HCL,  $X_{\text{HCL}}$ , %  
 (Wt. Fraction HCL,  $W_{\text{HCL}}$ )  
 Salt-Free Basis

$X_{\text{HCL}}$  (Wt. %)

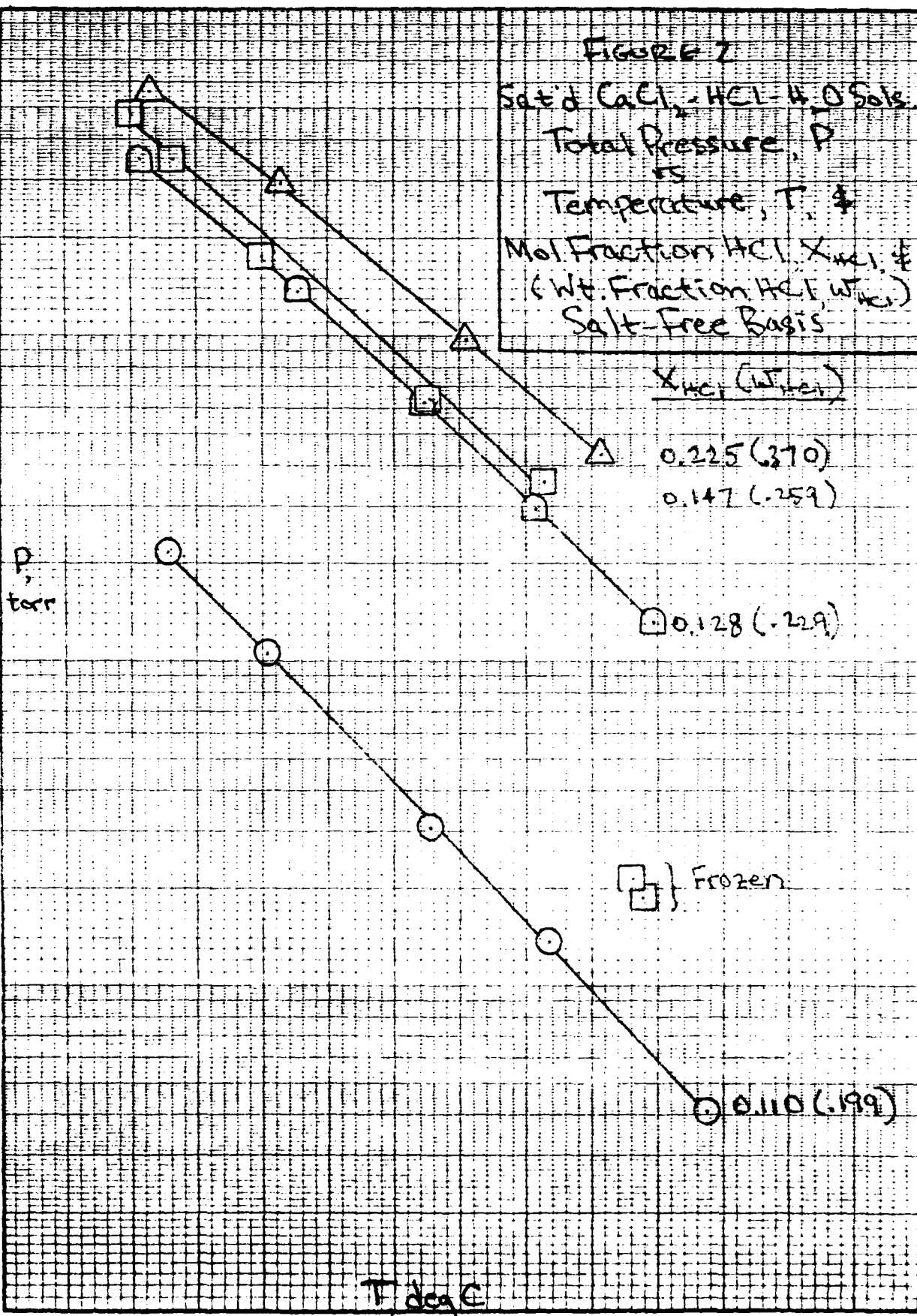
0.225 (37.0)

0.147 (25.9)

0.128 (22.9)

Frozen

0.110 (19.9)



P,  
torr

T, deg C

0.01

0

-10

-20

-30

-40

-50

100.0

Figure 3  
 Sat'd  $\text{CaCl}_2 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$  Sols  
 Partial Pressure  $\text{HCl}$ ,  $P_{\text{HCl}}$   
 vs  
 Temperature  $T$  &  
 Mol Fraction  $\text{HCl}$ ,  $X_{\text{HCl}}$ , &  
 (Wt Fraction  $\text{HCl}$ ,  $W_{\text{HCl}}$ )  
 Salt-Free Basis

$X_{\text{HCl}} (W_{\text{HCl}})$

0.225 (0.370)

0.147 (0.259)

0.128 (0.229)

$P_{\text{HCl}}$   
 Torr

$\square$  } Frozen

0.110 (0.199)

$T, \text{ deg C}$

0.01

0

10

-20

-30

-40

-50

NO 340-1410 DUTZGEN GRAPH PAPER  
 SEMI-LOGARITHMIC  
 4 CYCLES X 10 DIVISIONS PER INCH

NO 340-1410 DUTZGEN GRAPH PAPER  
 SEMI-LOGARITHMIC  
 4 CYCLES X 10 DIVISIONS PER INCH

100:10

9

8

7

6

5

4

3

2

1

10

9

8

7

6

5

4

3

2

1

1

0.8

0.6

0.4

0.2

0.1

0.08

0.06

0.04

0.02

0.01

 $P_{H_2O}$ ,  
torr $T, \text{deg C}$ 

0.01

-10

-20

-30

-40

-50

FIGURE 4

Sat'd  $\text{CaCl}_2$ - $\text{HCl}$ - $\text{H}_2\text{O}$  SolsPartial Pressure  $\text{H}_2\text{O}$ ,  $P_{H_2O}$ 

vs

Temperature,  $T$ ,  $^\circ\text{C}$ Mol Fraction  $\text{HCl}$ ,  $X_{\text{HCl}}$ ,  $\phi$ (Wt. fraction  $\text{HCl}$ ,  $w_{\text{HCl}}$ )

Salt-Free Basis

 $X_{\text{HCl}} (w_{\text{HCl}})$ 

0.225 (.370)

0.147 (.259)

0.128 (.229)

Frozen {  $\square$  0.110 (.199)

LMED  
-8







